

Approximate analytic solutions of the diatomic molecules in the Schrödinger equation with hyperbolical potentials

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Abstract

The Schrödinger equation for the rotational-vibrational (ro-vibrational) motion of a diatomic molecule with empirical potential functions is solved approximately by means of the Nikiforov-Uvarov method. The approximate ro-vibrational energy spectra and the corresponding normalized total wavefunctions are calculated in closed form and expressed in terms of the hypergeometric functions or Jacobi polynomials $P_n^{(\mu,\nu)}(x)$, where $\mu > -1$, $\nu > -1$ and $x \in [-1, +1]$. The s-waves analytic solution is obtained. The numerical energy eigenvalues for selected H_2 and Ar_2 molecules are also calculated and compared with the previous models and experiments.

Keywords: Diatomic molecules, ro-vibrational energy spectra, hyperbolical potentials, Nikiforov-Uvarov method

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I. INTRODUCTION

The problems connected with the molecular structure provide interesting and instructive applications of quantum mechanics, since molecules are considerably more complex in structure than atoms. Two distinct problems arise in connection with molecular structure. The first is to obtain the electronic wave functions and potential energy functions of the nuclear coordinates. This problem can be solved analytically only in the simplest cases. The second is to obtain the solution of the nuclear motion equation. In solving the second problem, the construction of a suitable potential function of a diatomic molecule is very important. It has been found that the potential-energy function for the lowest electronic states of actual diatomic molecules can be expressed by the Morse potential [1]:

$$V_M(r) = D [1 - \exp[-\alpha(r - r_e)]]^2, \quad (1)$$

which has three adjustable positive parameters α , D and r_e . At $r = r_e$, it has a minimum value at zero and approaches D exponentially for large r . If $\frac{1}{\alpha}$ is somewhat smaller than r_e , it becomes large (but not infinite) as $r \rightarrow 0$. This potential has been the subject of many studies since 1929 [1]. Also, it is an important potential in the field of molecular physics describing the interaction between two atoms and has attracted a great interest for some decades [1,2].

During the past years progress has been made in the field of diatomic molecules and extensive use of the potential functions have been introduced [3,4]. At present the Morse potential is still one of the potential functions used most in molecular physics and quantum chemistry [5]. However, the Morse potential has few asymptotic inaccuracies in the regions of small and large r . Obviously, unlike the true Coulombic interaction among two atoms which approaches infinity, the potential is finite when the distance of two atoms approaches zero. Another inaccuracy is the replacement of the Van der Waals term by an exponential which makes the value of the Morse potential smaller than that from the experiments in the region of large r . To avoid these inaccuracies, many works have been carried out in that direction to improve Morse potential [6].

In 1986, Schiöberg [7] suggested hyperbolical (empirical) potential functions of the form:

$$V_{\pm}(r) = D [\delta - \sigma [\coth(\alpha r)]^{\pm}]^2, \quad (2)$$

where D , α , δ , and σ are four adjustable positive parameter with $D = D_e/(\delta - \sigma)^2$ (D_e is

the spectroscopic dissociation energy). It is similar to Morse potential having the minimum value 0 at the point

$$r = r_e = \frac{1}{\alpha} \arctan h \left(\frac{\sigma}{\delta} \right)^{\pm}, \quad (3)$$

and approaches D exponentially for large r . The functional forms (2) are significant in the limits of $0 \leq \sigma < \delta$ for $V_+(r)$ and $\sigma < \delta \leq 0$ for $V_-(r)$. $V_+(r)$ becomes more and more asymmetric if one lowers the potential constants δ and σ but $V_-(r)$ becomes more and more symmetric with increasing δ and σ . One can change the potential constants of $V_{\pm}(r)$ in such a manner that the energy eigenvalues change into all known energy values which one obtains from rigorous quantum mechanical or semiclassical solutions. These are the energy values of the Morse, the Kratzer, the Coulomb, the harmonic oscillator and other potential functions. The Morse function represents the connection point between $V_+(r)$ and $V_-(r)$ [7]. Unlike the Morse potential (1), the empirical potential (EP) function $V_+(r)$ approaches infinity at the point $r = 0$. In the region of large r , it is closer to the experimental Rydberg-Klein-Rees (RKR) curve than the Morse potential for some diatomic molecules. This potential is not only a better description for the potential energy of a pure molecular vibrational (= radial) energies but it represents also perfectly intermolecular interactions and includes with the Kratzer energy eigenvalues the Rydberg terms of an electron in an atom. Besides, the semiclassically calculated term values for 'vibrations' in a plane there are also the quantum-mechanical calculated term values which include these radial terms and zero-point energies of a 'rotation' in space.

Recently, Lu [8] solved approximately the Schrödinger equation of diatomic molecules with the EP functions using the hypergeometric series method. Furthermore, rigorous solutions of the Schrödinger equation are also obtained with a similar method for zero total angular momentum. Since there are no exact analytic solutions for the EP functions ($l \neq 0$), some approximation [8] was used to obtain the solutions. This approximation was employed in solving the rotating Morse potential for any l -states [9,10]. The ro-vibrational energy eigenvalues of the EP functions were determined with a semiclassical (SC) procedure (the Bohr-Sommerfeld quantization condition) and a quantum-mechanical (QM) method (the Schrödinger equation) [8].

The NU method [11] and other methods have also been used to solve the non-relativistic and relativistic wave equations [12-14]. The purpose of this work is to solve the radial Schrödinger equation with any orbital angular quantum number l for EP functions $V_{\pm}(r)$

using a generalized model of the NU method derived for the exponential-type potentials like EP. In addition, we apply the analytic solution to obtain the ro-vibrational energy states for selected H_2 and Ar_2 diatomic molecules using the relevant potential parameters and spectroscopic constants given in Ref. [7].

The present work is organized as follows. In section 2, we present a parametric generalization of the NU method holds for any exponential-type potential. In section 3, we obtain the analytic NU bound state solution of the Schrödinger equation with the EP functions for any l -states. In Section 4, we calculate the ro-vibrational energy states for selected H_2 and Ar_2 diatomic molecules. Section 5 contains the relevant conclusions.

II. NU METHOD

The Nikiforov-Uvarov (NU) method is briefly outlined here and the details can be found in [11]. It is proposed to solve the second-order linear differential equation by reducing it to a generalized equation of hypergeometric-type of the following form:

$$R''(z) + \left(\frac{\tilde{\tau}(z)}{\sigma(z)} \right) R'(z) + \left(\frac{\tilde{\sigma}(z)}{\sigma^2(z)} \right) R(z) = 0, \quad (4)$$

where the prime denotes the differentiation with respect to z , $\sigma(z)$ and $\tilde{\sigma}(z)$ are polynomials, at most second-degree, and $\tilde{\tau}(s)$ is a first-degree polynomial. In order to find a particular solution of Eq. (4), we decompose the wavefunction $R(z)$ as follows:

$$R(z) = \phi(z)y_n(z), \quad (5)$$

which reduces Eq. (4) to a hypergeometric type equation

$$\sigma(z)y_n''(z) + \tau(z)y_n'(z) + \lambda y_n(z) = 0, \quad (6)$$

where $\phi(z)$ is defined as a logarithmic derivative

$$\phi'(z)/\phi(z) = \pi(z)/\sigma(z), \quad (7)$$

and the other part $y_n(z)$ is the hypergeometric-type function whose polynomial solution satisfies the Rodrigues relation:

$$y_n(z) = \frac{A_n}{\rho(z)} \frac{d^n}{dz^n} [\sigma^n(z)\rho(z)], \quad (8)$$

where A_n is a normalizing factor and $\rho(z)$ is the weight function satisfying the condition

$$(\sigma(z)\rho(z))' = \tau(z)\rho(z). \quad (9)$$

The function $\pi(z)$ and the eigenvalue λ required in this method are defined as

$$\pi(z) = \frac{1}{2} [\sigma'(z) - \tilde{\tau}(z)] \pm \sqrt{\frac{1}{4} [\sigma'(z) - \tilde{\tau}(z)]^2 - \tilde{\sigma}(z) + k\sigma(z)}. \quad (10)$$

and

$$\lambda = k + \pi'(z). \quad (11)$$

Hence, the determination of k is the essential point in the calculation of $\pi(z)$, for which the discriminant of the square root in Eq. (10) is set to zero. Also, the eigenvalue equation defined in Eq. (11) takes the following new form

$$\lambda = \lambda_n = -n\tau'(z) - \frac{1}{2}n(n-1)\sigma''(z), \quad n = 0, 1, 2, \dots. \quad (12)$$

where

$$\tau(z) = \tilde{\tau}(z) + 2\pi(z), \quad (13)$$

and its derivative is negative (i.e., $\tau'(z) < 0$) which is the essential condition for any choice of proper bound-state solutions. Finally, comparing Eqs. (11) and (12), we obtain the energy eigenvalues.

In this regard, we can derive a parametric generalization of the NU method valid for any central and non-central exponential-type potential [12]. We begin by comparing comparing the following generalized hypergeometric-type equation

$$R''(z) + \frac{(c_1 - c_2z)}{z(1 - c_3z)}R'(z) + \frac{1}{[z(1 - c_3z)]^2}(-\xi_1z^2 + \xi_2z - \xi_3)R(z) = 0, \quad (14)$$

with Eq. (4), we obtain

$$\tilde{\tau}(z) = c_1 - c_2z, \quad (15a)$$

$$\sigma(z) = z(1 - c_3z) \quad (15b)$$

$$\tilde{\sigma}(z) = -\xi_1z^2 + \xi_2z - \xi_3. \quad (15c)$$

Further, substituting Eqs. (15a)-(15c) into Eq. (10), we find

$$\pi(z) = c_4 + c_5z \pm [(c_6 - c_3k_{+,-})z^2 + (c_7 + k_{+,-})z + c_8]^{1/2}, \quad (16)$$

where

$$c_4 = \frac{1}{2}(1 - c_1), \quad c_5 = \frac{1}{2}(c_2 - 2c_3), \quad c_6 = c_5^2 + \xi_1, \quad c_7 = 2c_4c_5 - \xi_2, \quad c_8 = c_4^2 + \xi_3. \quad (17)$$

The discriminant under the square root sign in Eq. (16) must be set to zero and the resulting equation has to be solved for k , it yields

$$k_{+,-} = -(c_7 + 2c_3c_8) \pm 2\sqrt{c_8c_9}, \quad (18)$$

where

$$c_9 = c_3(c_7 + c_3c_8) + c_6. \quad (19)$$

Substituting Eq. (18) into Eq. (16) and then solving, we obtain the physical choice of parameters:

$$\pi(z) = c_4 + c_5z - [(\sqrt{c_9} + c_3\sqrt{c_8})z - \sqrt{c_8}], \quad (20)$$

$$k_- = -(c_7 + 2c_3c_8) - 2\sqrt{c_8c_9}. \quad (21)$$

In addition, Eqs. (13), (15) and (20) provide the parameter

$$\tau(z) = 1 - (c_2 - 2c_5)z - 2[(\sqrt{c_9} + c_3\sqrt{c_8})z - \sqrt{c_8}], \quad (22)$$

whose derivative must be negative:

$$\tau'(z) = -2c_3 - 2(\sqrt{c_9} + c_3\sqrt{c_8}) < 0, \quad (23)$$

in accordance with essential requirement of the method [11]. Solving Eqs. (11) and (12), we obtain the parametric energy equation:

$$(c_2 - c_3)n + c_3n^2 - (2n + 1)c_5 + (2n + 1)(\sqrt{c_9} + c_3\sqrt{c_8}) + c_7 + 2c_3c_8 + 2\sqrt{c_8c_9} = 0, \quad (24)$$

for the exponential-type potential under study. Let us now turn to the calculations of the wavefunctions. The weight function $\rho(z)$ can be calculated by means of Eq. (9) as

$$\rho(z) = z^{c_{10}}(1 - c_3z)^{c_{11}}, \quad (25)$$

and consequently the first part of the wavefunctions throughout the Rodrigues relation (8):

$$y_n(z) = P_n^{(c_{10}, c_{11})}(1 - 2c_3z), \quad c_{10} > -1, \quad c_{11} > -1, \quad z \in [0, 1/c_3], \quad (26)$$

where

$$c_{10} = c_1 + 2c_4 + 2\sqrt{c_8} - 1 > -1, \quad c_{11} = 1 - c_1 - 2c_4 + \frac{2}{c_3}\sqrt{c_9} > -1, \quad (27)$$

and $P_n^{(a,b)}(1 - 2c_3z)$ are the Jacobi polynomials. Also, the second part of the wavefunctions can be found from (7) as

$$\phi(z) = z^{c_{12}}(1 - c_3z)^{c_{13}}, \quad c_{12} > 0, \quad c_{13} > 0, \quad (28)$$

where

$$c_{12} = c_4 + \sqrt{c_8} > 0, \quad c_{13} = -c_4 + \frac{1}{c_3}(\sqrt{c_9} - c_5) > 0. \quad (29)$$

Hence, the general wavefunction (5) has the general form

$$R(z) = \mathcal{N}_n z^{c_{12}}(1 - c_3z)^{c_{13}} P_n^{(c_{10}, c_{11})}(1 - 2c_3z), \quad (30)$$

where \mathcal{N}_n is a normalization constant.

III. BOUND STATES OF THE HYPERBOLICAL POTENTIALS

The Schrödinger equation for diatomic molecules with hyperbolic potential functions takes the form:

$$\left\{ \nabla^2 + \frac{2\mu}{\hbar^2} [E_{nl} - V_{\pm}(r)] \right\} \psi_{nlm}(r, \theta, \varphi) = 0, \quad (31)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$. The wavefunctions in the above equation could be separated to the following form [15-18]

$$\psi_{nlm}(r, \theta, \varphi) = \frac{1}{r} R_{nl}(r) Y_{lm}(\theta, \varphi), \quad (32)$$

where $Y_{lm}(\theta, \varphi)$ is a spherical harmonic with angular momentum quantum numbers l and m . The substitution of Eq. (32) into Eq. (31) gives the following radial reduced wave function $R_{nl}(r)$ satisfying

$$\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2} [E_{nl} - V_{\pm}(r)] \right\} R_{nl}(r) = 0, \quad (33)$$

where $\frac{l(l+1)}{r^2}$ is the centrifugal potential with the boundary condition that $R_l(r)$ vanishes near the points $r = 0$ and $r \rightarrow \infty$. Furthermore, if l is not too large, the case of the vibrations of small amplitude about the minimum, we can then use the approximate expansion of the centrifugal potential near the minimum point $r = r_e$ as [19]:

$$\frac{l(l+1)}{r^2} \approx \frac{l(l+1)}{r_e^2} \left\{ A_0 + A_1 \frac{\pm \exp(-2\alpha r)}{1 \mp \exp(-2\alpha r)} + A_2 \left[\frac{\pm \exp(-2\alpha r)}{1 \mp \exp(-2\alpha r)} \right]^2 \right\}, \quad (34)$$

where

$$A_0 = 1 - \left[\frac{1 \mp \exp(-2\alpha r_e)}{2\alpha r_e} \right]^2 \left[\frac{8\alpha r_e}{1 \mp \exp(-2\alpha r_e)} - (3 + 2\alpha r_e) \right], \quad (35a)$$

$$A_1 = \pm 2 [\exp(2\alpha r_e) \mp 1] \left\{ 3 \left[\frac{1 \mp \exp(-2\alpha r_e)}{2\alpha r_e} \right] - (3 + 2\alpha r_e) \left[\frac{1 \mp \exp(-2\alpha r_e)}{2\alpha r_e} \right]^2 \right\}, \quad (35b)$$

$$A_2 = [\exp(2\alpha r_e) \mp 1]^2 \left[\frac{1 \mp \exp(-2\alpha r_e)}{2\alpha r_e} \right]^2 \left[3 + 2\alpha r_e - \frac{4\alpha r_e}{1 \mp \exp(-2\alpha r_e)} \right], \quad (35c)$$

and higher order terms are neglected. In fact, Eq. (34) is the approximate expansion of the centrifugal potential $l(l+1)r^{-2}$ and is valid for all $r \approx r_e$, the minimum point of $V_{\pm}(r)$ since r is not singular there. However, the expansion is not valid near the singularity point $r = 0$. Overmore, it is a good approximation for small vibrations around the equilibrium separation $r - r_e$.

Substituting Eqs. (2) and (34) into Eq. (33) and introducing a new variable $z = \pm \exp(-2\alpha r)$, where $z \in [\pm 1, 0]$ for $V_{\pm}(r)$, we obtain the hypergeometric-type wave equation:

$$R''_{nl}(z) + \frac{(1-z)}{z(1-z)} R'_{nl}(z) + \frac{1}{z^2(1-z)^2} \times \left[- \left(K_{nl}^2 + S_l^2 - Q_l - \frac{1}{4} \right) z^2 + (2K_{nl}^2 - Q_l) z - K_{nl}^2 \right] R_{nl}(z) = 0, \quad (36)$$

where $R_{nl}(z) = R_{nl}(r)$ and

$$K_{nl} = \sqrt{\frac{\mu D}{2\alpha^2 \hbar^2} (\delta - \sigma)^2 + \frac{l(l+1)}{4\alpha^2 r_e^2} A_0 - \frac{\mu E_{nl}}{2\alpha^2 \hbar^2}}, \quad (37a)$$

$$Q_l = -\frac{2\mu D}{\alpha^2 \hbar^2} \sigma (\delta - \sigma) + \frac{l(l+1)}{4\alpha^2 r_e^2} A_1, \quad (37b)$$

$$S_l = \sqrt{\frac{2\mu D}{\alpha^2 \hbar^2} \sigma^2 + \frac{l(l+1)}{4\alpha^2 r_e^2} A_2 + \frac{1}{4}}. \quad (37c)$$

By comparing Eq. (36) with Eq. (14), we obtain specific values for the set of constant parameters given in Section 2:

$$\begin{aligned} c_1 = c_2 = c_3 = 1, \quad c_4 = 0, \quad c_5 = -\frac{1}{2}, \quad c_6 = K_{nl}^2 + S_l^2 - Q_l, \\ c_7 = -2K_{nl}^2 + Q_l, \quad c_8 = K_{nl}^2, \quad c_9 = S_l^2, \\ c_{10} = 2K_{nl}, \quad c_{11} = 2S_l, \quad c_{12} = K_{nl}, \quad c_{13} = S_l + \frac{1}{2}, \\ \xi_1 = K_{nl}^2 + S_l^2 - Q_l - \frac{1}{4}, \quad \xi_2 = 2K_{nl}^2 - Q_l, \quad \xi_3 = K_{nl}^2. \end{aligned} \quad (38)$$

By using Eqs. (20)-(22), we find the following physical values:

$$\pi(z) = K_{nl} - \left(\frac{1}{2} + K_{nl} + S_l \right) z, \quad (39)$$

$$k = -Q_l - 2K_{nl}S_l, \quad (40)$$

$$\tau(z) = 1 + 2K_{nl} - 2(1 + K_{nl} + S_l)z, \quad (41)$$

where $\tau'(z) = -2(1 + K_{nl} + S_l) < 0$ is the essential condition for bound-state (real) solutions. In addition, the energy equation can be found via Eq. (24) as

$$2K_{nl} = \frac{S_l^2 - Q_l - \frac{1}{4} - (S_l + n + \frac{1}{2})^2}{S_l + n + \frac{1}{2}}. \quad (42)$$

The energy eigenvalues are obtained as follows,

$$E_{nl} = D(\delta - \sigma)^2 + \frac{l(l+1)\hbar^2}{2\mu r_e^2} A_0 - \frac{\hbar^2 \alpha^2}{2\mu} \left[\frac{S_l^2 - Q_l - \frac{1}{4} - (S_l + n + \frac{1}{2})^2}{S_l + n + \frac{1}{2}} \right]^2, \quad n, l = 0, 1, 2, \dots,$$

where n and l signify the usual vibrational and rotational quantum numbers, respectively.

Thus, the ro-vibrational energy spectrum takes the following explicit form

$$E_{nl} = D_e + \frac{l(l+1)\hbar^2}{2\mu r_e^2} A_0 - \frac{\hbar^2 \alpha^2}{2\mu} \left[\frac{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma \delta + \frac{l(l+1)}{4\alpha^2 r_e^2} (A_2 - A_1) - \left(n + \frac{1}{2} + \sqrt{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma^2 + \frac{l(l+1)}{4\alpha^2 r_e^2} A_2 + \frac{1}{4}} \right)^2}{n + \frac{1}{2} + \sqrt{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma^2 + \frac{l(l+1)}{4\alpha^2 r_e^2} A_2 + \frac{1}{4}}} \right]^2, \quad (43)$$

which is identical to Eq. (28) of Ref. [8]. Its important to mention that very similar expressions to the above expression for the energy states have been found over the past years for the hypebolical (exponential-type) potentials with δ is being set equal to one in Eq. (2) (cf. [19-21]). Very recently, a new improved approximation [21,22] for the centrifugal potential term $l(l+1)/r^2$ was used different than the ones used in Ref. [8] and the one which is commonly used in literature by Ref. [23].

Let us now turn to the calculations of the corresponding wavefunctions for the EP functions. Thus, referring to the parametric generalization of the NU method in Section 2, the weight function in Eq. (25) takes the form

$$\rho(z) = z^{2K_{nl}}(1-z)^{2S_l}, \quad (44)$$

which gives the first part of the wavefunctions in Eq. (5) as

$$y_n(z) \rightarrow P_n^{(2K_{nl}, 2S_l)}(1 - 2z). \quad (45)$$

Also, the second part of the wavefunctions (28) can be found as

$$\phi(z) \rightarrow z^{K_{nl}}(1 - z)^{S_l + \frac{1}{2}}. \quad (46)$$

Hence, the unnormalized wavefunctions (30) are being expressed in terms of the Jacobi polynomials as

$$R_{nl}(z) = \mathcal{N}_{nl} z^{K_{nl}} (1 - z)^{S_l + \frac{1}{2}} P_n^{(2K_{nl}, 2S_l)}(1 - 2z), \quad (47)$$

where \mathcal{N}_{nl} is a normalizing factor and $P_n^{(2K_{nl}, 2S_l)}(1 - 2z) = \frac{(2K_{nl}+1)_n}{n!} {}_2F_1(-n, 2K_{nl} + 2S_l + n + 1, 2K_{nl} + 1; z)$ with $(m)_n = \frac{(m+n-1)!}{(m-1)!}$ is Pochhammer's symbol.

Hence, the total wavefunctions of the EP are

$$\begin{aligned} \psi_{\pm}(r, \theta, \varphi) &= \mathcal{N}_{nl} \frac{1}{r} [\pm \exp(-2\alpha r)]^{K_{nl}} [1 - \pm \exp(-2\alpha r)]^{S_l + \frac{1}{2}} \\ &\times P_n^{(2K_{nl}, 2S_l)}(1 - \pm 2 \exp(-2\alpha r)) Y_{lm}(\theta, \varphi). \end{aligned} \quad (48)$$

where the normalization constants \mathcal{N}_{nl} are determined in Appendix A.

Let us find the vibrational energy states for the s -waves ($l = 0$) from Eq. (43) as

$$E_n = D_e - \frac{\hbar^2 \alpha^2}{2\mu} \left[\frac{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma \delta - \left(\sqrt{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma^2 + \frac{1}{4}} + n + \frac{1}{2} \right)^2}{\sqrt{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma^2 + \frac{1}{4}} + n + \frac{1}{2}} \right]^2, \quad n = 0, 1, 2, \dots, n_{\max}, \quad (49)$$

where n_{\max} is the number of bound states for the whole bound spectrum near the continuous zone. n_{\max} is the largest integer which is less than or equal to the value of n that makes the right side of Eq. (49) vanish, that is,

$$n_{\max} = \frac{1}{2} \left(\sqrt{\frac{8\mu D}{\hbar^2 \alpha^2} \sigma \delta} - \sqrt{\frac{8\mu D}{\hbar^2 \alpha^2} \sigma^2 + 1} - 1 \right). \quad (50)$$

Thus, n_{\max} cannot be infinite ($E_{n_{\max}} = D_e$), which is reflected in the above condition. Furthermore, the corresponding wavefunctions for the s -waves can be easily found from Eqs. (37) and (48) as

$$\begin{aligned} \psi_{\pm}(r, \theta, \varphi) &= \mathcal{N}_n \frac{1}{r} [\pm \exp(-2\alpha r)]^{k_n} [1 - \pm \exp(-2\alpha r)]^{s + \frac{1}{2}} \\ &\times P_n^{(2k_n, 2s)}(1 - \pm 2 \exp(-2\alpha r)) Y_{0,0}(\theta, \varphi), \end{aligned} \quad (51)$$

where the normalization constants \mathcal{N}_n are determined in Appendix A.

IV. APPLICATIONS TO DIATOMIC MOLECULES

In this section, we calculate the energy states for the two selected H_2 and Ar_2 diatomic molecules using Eqs. (35) and (43). The spectroscopic constants of these two molecules are given in Table 1. The vibrating ground state energy eigenvalues E_+^{00} (in cm^{-1}) for the H_2 molecule in the EP functions $V_+(r)$ are found by means of parametric generalization version of the NU method for the potential parameters given in Table 2. Our numerical results obtained in the present NU model are listed together with the analogous numerical results obtained by using SC procedure and a QM method mentioned in Ref. [7] for various potential parameters. Obviously, as shown in Table 2, the results obtained in the present model are in high agreement with those obtained by QM, however, the SC procedure is proportionally different. Therefore, the differences between our results and SC procedure are less than 0.01 cm^{-1} , i.e., they are negligible because of these approximations: $1\text{ a.m.u} = 931.502\text{ MeV}/c^2$, $1\text{ cm}^{-1} = 1.23985 \times 10^{-4}\text{ eV}$ and $\hbar c = 1973.29\text{ eV}\cdot\text{\AA}^\circ$ [28]. The second application is applied to Ar_2 molecule. We confine our study to calculate the ro-vibrating energy states for the $V_+(r)$ potential using the the following potential parameters: $\sigma = 25.23$, $\delta = 41.75$ and $\alpha = 0.6604\text{ (}\text{\AA}^\circ\text{)}^{-1}$ [7] together with the parameters given in Table 1. The splittings of the energy states of s -waves $E_+ = E_+(n \neq 0) - E_+(n = 0)$ obtained by the NU method and SC procedures are presented in Table 3. The present results $\Delta E_+(NU)$ from NU method and $\Delta E_+(SC)$ obtained from the SC procedures are also compared with four-different experimental results labeled by $\Delta E(a)$, $\Delta E(b)$, $\Delta E(c)$ and $\Delta E(d)$ taken from Ref. [7]. It is clear from Table 3 that our results are very close with the expremimentally determined values as well as the SC procedure results. Finally, the approximated ro-vibrating energy states of the $V_+(r)$ given in Eq. (2) for the Ar_2 and H_2 molecules are also calculated for the $l \neq 0$ case. Table 4 shows the energy levels for vibrational ($n = 0, 1, 2, 3, 4, 5$) and rotational ($l = 0, 1, 2$) quantum numbers.

V. CONCLUSIONS

In the present work, we have used a parametric generalization version of the NU method derived for any exponential-type potential to obtain the approximate solutions of the Schrödinger equation with any orbital angular momentum quantum number l for the hyper-

bolical (EP) functions. This method is systematical and efficient in finding the ro-vibrating energy states of a diatomic molecule and the normalized wave functions expressed in terms of the Jacobi polynomials. Obviously, the energy eigenvalues equation given in Eq. (43), considering the approximation in Eq. (35), is identical to those obtained by functional analysis method [8]. The analytical result is tested in calculating the ro-vibrating energy states of the H_2 and Ar_2 molecules. Comparisons with the results of previous methods SC and QM for the ground state ($n = l = 0$) show that our calculations are in high agreement with those experimental results for H_2 and Ar_2 for low values of the ro-vibrating energy states, i.e., $l = 0, 1, 2$. These systematical procedures could be useful for other molecular potentials in calculating their higher or lower approximated energy states [29-31].

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APPENDIX A: NORMALIZATION OF THE RADIAL WAVE FUNCTION

In order to find the normalization constants \mathcal{N}_{nl} , we start by writting the normalization condition:

$$\mathcal{N}_{nl}^{-2} = \frac{1}{2\alpha} \int_0^1 z^{2K_{nl}-1} (1-z)^{2S_l+1} [P_n^{(2K_{nl}, 2S_l)}(1-2z)]^2 dz. \quad (A1)$$

Unfortunately, there is no formula available to calculate this key integration. Nevertheless, we can find the explicit normalization constants \mathcal{N}_{nl} . For this purpose, it is not difficult to obtain the results of the above integral by using the following formulas [24-27,29-31]

$$\int_0^1 (1-z)^{\mu-1} z^{\nu-1} {}_2F_1(\alpha, \beta; \gamma; az) dz = \frac{\Gamma(\mu)\Gamma(\nu)}{\Gamma(\mu+\nu)} {}_3F_2(\nu, \alpha, \beta; \mu+\nu; \gamma; a), \quad (A2)$$

and ${}_2F_1(a, b; c; z) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} \sum_{p=0}^{\infty} \frac{\Gamma(a+p)\Gamma(b+p)}{\Gamma(c+p)} \frac{z^p}{p!}$. Following Ref. [24-27,29-31], we calculate the normalization constants:

$$\mathcal{N}_{nl} = \left[\frac{\Gamma(2K_{nl}+1)\Gamma(2S_l+2)}{2\alpha\Gamma(n)} \sum_{m=0}^{\infty} \frac{(-1)^m (1+n+2(K_{nl}+S_l))_m \Gamma(n+m)}{m! (m+2K_{nl})! \Gamma(m+2(K_{nl}+S_l+1))} f_{nl} \right]^{-1/2}, \quad (A3)$$

where

$$f_{nl} = {}_3F_2 \left(2K_{nl} + m, -n, n + 1 + 2(K_{nl} + S_l); m + 2(K_{nl} + S_l + 1); 1 + 2K_{nl}; 1 \right). \quad (\text{A4})$$

Furthermore, the normalization constants for the s -wave can be also found as

$$\mathcal{N}_n = \left[\frac{\Gamma(2k_n + 1)\Gamma(2s + 2)}{2\alpha\Gamma(n)} \sum_{m=0}^{\infty} \frac{(-1)^m (1 + n + 2(k_n + s))_m \Gamma(n + m)}{m! (m + 2k_n)! \Gamma(m + 2(k_n + s + 1))} g_n \right]^{-1/2}, \quad (\text{A5})$$

where

$$g_n = {}_3F_2 \left(2k_n + m, -n, n + 1 + 2(k_n + \widetilde{s}); m + 2(k_n + s + 1); 1 + 2k_n; 1 \right), \quad (\text{A6})$$

and

$$k_n = \sqrt{\frac{\mu D}{2\hbar^2 \alpha^2} (\delta - \sigma)^2 - \frac{\mu E_n}{2\hbar^2 \alpha^2}}, \quad s = \sqrt{\frac{2\mu D}{\hbar^2 \alpha^2} \sigma^2 + \frac{1}{4}}, \quad n = 0, 1, 2, \dots, \quad (\text{A7})$$

where E_n is given by Eq. (49).

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- [1] P.M. Morse, Phys. Rev. 34 (1929) 57; A. Lopez Piñeiro and B. Moreno, J. Chem. Phys. 87 (1987) 520; D. Popov, Phys. Scr. 63 (2001) 257; S.H. Dong, R. Lemus and A. Frank, Int. J. Quantum Phys. 86 (2002) 433.
- [2] M.S. Child and L. Halonen, Adv. Chem. Phys. 62 (1984) 1; L. Pauling and E.B. Wilson Jr., Introduction to Quantum Mechanics with Applications to Chemistry, Dover, New York, 1985.
- [3] G. Herzberg, Molecular Spectra and Molecular Structure, Van Nostrand, Princeton, N. J., 1950; J. Goodisman, Diatomic Interaction Potential Theory, Vols. 1 and 2, Academic Press, New York, 1953; J.N. Murrell, S. Carter and S.C. Farantos, Molecular potential Energy Functions, John Wiley and Sons, Chichester, 1984.
- [4] D.T. Haar, Phys. Rev. 70 (1946) 222; E.M. Greenawalt and A.S. Dickinson, J. Mol. Spectra 30 (1969) 427; B.W. Shore, J. Chem. Phys. 59 (1973) 6450; H. Taseli, J. Phys. A: Math. Gen. 31 (1998) 779; M. Znojil, Phys. Lett. A 264 (1999) 108; S. Yang and M.E. Kellman, Phys. Rev. A 65 (2002) 034103.
- [5] S. Flügge, P. Walgner and A. Weiguny, J. Mol. Spectra 23 (1967) 243; R.N. Kesarwani and Y.P. Varshni, Can. J. Phys. 58 (1980) 363; H. Konwent et al., J. Phys. A: Math. Gen. 31 (1998) 7541; E.D. Davis, Phys. Rev. A 70 (2004) 032101.
- [6] R. Zhang and C. Deng, Phys. Rev. A 47 (1993) 71; M. Molski, Phys. Rev. A 60 (1999) 3300; O.I. Tolstikhin and M. Matsuzawa, Phys. Rev. A 63 (2001) 062705; S. Andersson and N. Elander, Phys. Rev. A 69 (2004) 052507.
- [7] D. Schiöberg, Mol. Phys. 59 (1986) 1123.
- [8] J. Lu, Phys. Scr. 72 (2005) 349.
- [9] C. Berkdemir and J. Han, Chem. Phys. Lett. 409 (2005) 203; C. Berkdemir, Nucl. Phys. A 770 (2006) 32.
- [10] W.C. Qiang and S.H. Dong, Phys. Lett. A 363 (2007) 169.
- [11] A.F. Nikiforov and V.B. Uvarov, Special Functions of Mathematical Physics (Birkhauser, Basel, 1988).
- [12] S.M. Ikhdair, Eur. Phys. J. A 40 (2) (2009) 143; S.M. Ikhdair and R. Sever, to appear in the Cent. Eur. J. Phys. (2010) [DOI: 10.2478/s11534-009-0118-5].
- [13] S.M. Ikhdair and R. Sever, Ann. Phys. (Leipzig) 16 (2007) 218; S.M. Ikhdair and R. Sever,

- Int. J. Theor. Phys. 46 (2007) 1643; S.M. Ikhdaire and R. Sever, J. Math. Chem. 42 (2007) 461.
- [14] S.M. Ikhdaire, Chin. J. Phys. 46 (2008) 291; S.M. Ikhdaire and R. Sever, Ann. Phys. (Berlin) 17 (2008) 897; Cent. Eur. J. Phys. 6 (2008) 141, 685; Int. J. Mod. Phys. C 19 (2008) 221, 1425.
- [15] S.M. Ikhdaire and R. Sever, Z. Phys. C 56 (1992) 155; C 58 (1993) 153; D 28 (1993) 1.
- [16] S.M. Ikhdaire and R. Sever, Int. J. Mod. Phys. A 18 (2003) 4215; A 20 (2005) 4035; A 21 (2006) 2191, 6699; S. Ikhdaire *et al.*, Tr. J. Phys. 16 (1992) 510; 17 (1993) 474.
- [17] S.M. Ikhdaire and R. Sever, Int. J. Mod. Phys. A 19 (2004) 1771; A 20 (2005) 6509; S.M. Ikhdaire and R. Sever, Int. J. Mod. Phys. E 17 (2008) 669; S.M. Ikhdaire, to appear in Int. J. Mod. Phys. A 24 (2009) [arXiv:0904.1665].
- [18] M.N. Nieto, Am. J. Phys. 47 (1979) 1067.
- [19] J. Lu, H.-X. Qian, L.-M. Li and F.-L. Liu, Chin. Phys. 14 (2005) 2402.
- [20] S. Dong, J. Garcia-Ravelo and S.-H. Dong, Phys. Scr. 76 (2007) 393.
- [21] S.M. Ikhdaire and R. Sever, Ann. Phys. (Berlin) 18 (4) (2009) 189.
- [22] S.M. Ikhdaire, Eur. Phys. J. A 39 (3) (2009) 307; S.M. Ikhdaire and R. Sever, Phys. Scr. 79 (3) (2009) 035002.
- [23] S.M. Ikhdaire, Int. J. Mod. Phys. C 20 (1) (2009) 25; S.M. Ikhdaire and R. Sever, Int. J. Mod. Phys. C 20(3) (2009) 361.
- [24] I.S. Gradshteyn and I.M. Ryzhik, Tables of Integrals, Series, and Products, 5th edn (New York, Academic, 1994).
- [25] G. Szego, Orthogonal Polynomials, (American Mathematical Society, New York, 1939).
- [26] W. Magnus, F. Oberhettinger and R.P. Soni, Formulas and Theorems for the Special Function of Mathematical Physics, 3rd Ed., (Berlin, Springer, 1966).
- [27] M. Abramowitz and I.A. Stegun, Handbook of Mathematical Functions (Dover, New York, 1964); A.P. Prudnikov, Yu.A. Brychkov and O.I. Marichev, Integrals and Series, (New York, Gordon and Breach, 1986).
- [28] B.H. Brandsen and C.J. Joachain, Quantum Mechanics, 2nd edn., Pearson Education Ltd., England.
- [29] S.M. Ikhdaire, Chem. Phys. 361 (1-2) (2009) 9.
- [30] S.M. Ikhdaire, to appear in the Int. J. Mod. Phys. C 20 (10) (2009) [arXiv:0905.2867].
- [31] S.M. Ikhdaire and R. Sever, J. Math. Chem. 45(4) (2009) 1137.

TABLE I: The spectroscopic constants of the EP.for H_2 and Ar_2 molecules [7].

Parameters	H_2	Ar_2
D_e (cm^{-1})	38281	99.55
r_e (A°)	0.7414	3.759
μ (a.m.u)	0.50407	19.9812

TABLE II: The EP parameters of the $V_+(r)$ and the ground state energy, E_+^{00} (in cm^{-1}) of the H_2 molecule.

σ	δ	α (A°) $^{-1}$	$E_+(SC)$	$E_+(QM)$	Present
426.826	463.102	0.9327	2167.68	2168.93	2168.68
47.294	102.341	0.6146	2153.69	2164.83	2164.45
28.685	117.121	0.3826	2139.57	2157.69	2157.53
21.250	213.212	0.1762	2124.29	2148.40	2147.53

TABLE III: Comparisons of experimentally calculated s -states energy transition values $\Delta E_{n,0}(cm^{-1})$ for $n \neq 0 \rightarrow n = 0$ together with the results of the SC procedure and the present NU method for the Ar_2 molecule.

n	Present	$\Delta E(a)$	$\Delta E(b)$	$\Delta E(c)$	$\Delta E(d)$	$\Delta E_+(SC)$
1	25.808	25.74	25.49	25.21	25.56	25.75
2	46.079	46.15	45.63	45.02	46.00	46.01
3	61.472	61.75	60.70	60.04	61.32	61.42
4	72.536	72.66	71.33	70.92	71.52	72.52
5	79.733	79.44	-	-	-	79.79
6	83.453	-	-	-	-	83.59
7	84.026	-	-	-	-	-

TABLE IV: Energy levels $E_{n,l}(cm^{-1})$ for Ar_2 and H_2 molecules in $V_+(r)$ using the NU method.

n	l	$E_+(Ar_2)$	$E_+(H_2)$
0	0	15.3828	2168.68
1	0	41.1910	6306.66
	1	25.7584	6331.10
2	0	61.4619	10183.8
	1	49.7874	10207.6
	2	-	10255.2
3	0	76.8546	13802.1
	1	68.3028	13825.2
	2	19.9133	13871.5
4	0	87.9188	17163.2
	1	82.0041	17185.7
	2	46.4777	17230.7
5	0	95.1159	20269.1
	1	91.4672	20291.0
	2	66.5474	20334.8